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Determination of phosphorus in steel by precipitation as silverphosphate and subsequent determination by spectrophotometric method

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Abstract: Presence of phosphorus in steel is due to impurities coming from iron making process. Phosphorous in steel has been determined by dissolution in 1:1 (v/v) HNO_3 followed by complexation of iron matrix by EDTA at pH 4. Phosphorus is precipitated with silver nitrate solution producing a yellow colored silver orthophosphate (Ag_3PO_4). The precipitate is redissolved in dilute nitric acid (1:10 v/v). A complex of phospho-vanado-molybdic acid is formed which is measured (440 nm) colorimetrically. Interference from Cr(VI) is eliminated by reducing it to Cr(III). Tungsten interferes in the estimation, whereas, vanadium (5 wt. %) and molybdenum (1.5 wt. %) containing steel can be estimated. Several BCS steel samples have been estimated with RSD value of 4.0%. This method has been applied in the chemical analysis of several steel samples submitted to the laboratory. The results were compared with IS and ASTM method of analysis and the RSD value of analysis is between ±4.0 %.

Keywords : Phosphorus determination, steel, silverphosphate separation, colorimetric estimation, spectrophotometric method.

INTRODUCTION

Phosphorus estimation in steel is conveniently done both by conventional and instrumental method of analysis. Both the techniques involve separation of phosphorus from interfering elements present in the matrix with subsequent detection in a suitable form. In conventional technique the sample is dissolved in acid and phosphorus precipitated as ammonium phosphomolybdate. It is either reprecipitated as $PbMoO_4$ and by determining the molybdenum content phosphorus is estimated or ammonium phospho-molybdate is dissolved in a given amount of excess of alkali and the remainder is titrated. Phosphorus is estimated from the amount of alkali consumed. Otherwise, this complex is reduced and measured colorimetrically[1-3].

Amongst instrumental technique of analysis for phosphorus, the atomic absorption spectroscopy (AAS), absorption in visible range are widely used although neutron activation and ICP-OES has also been applied by some workers. The determination of phosphorus in steel by graphite furnace AAS is plagued by a spectral interference. Voellkopf et al.[4] used a 0.2% lanthanum solution as matrix modifier and Zeeman background correction using an alternating transverse magnetic field at the furnace which eliminated the problem and allows a routine determination of phosphorus down to 0.002% in steel. Shkinev et al.[5] extracted phosphate ion with dialkyltin forming an innersphere complexes with the extracted anion. They reviewed the extraction/atomic absorption determinations of arsenic and phosphorus in metals and alloys. Ramchandran & Gupta[6] extracted a bismuthophospho-molybdate complex by methyl isobutyl ketone and determined bismuth by atomic-absorption spectrophotometry and

correlated with the phosphorus content. Kirkbright et al.[7] detected phosphorus by ICP-AES in aqueous solutions as anions. They Optimised the parameters of detection of phosphorus at 213.62 nm with a detection limit of 0.08 ppm. McLeod et al.[8] interfaced a microcolumn of activated alumina having a high affinity for phosphate ions in a flow injection analysis (FIA) system coupled to an ICP-AES instrument for performing rapid analyte enrichment/matrix removal .The system was tested for the determination of trace phosphorus in synthetic aqueous solutions utilising the PI 213.62 nm. Wittmann et al.[9] removed interference by the line coincidence of copper by bonding phosphorus in a vanado-molybdic complex molecule and by analysing molybdenum. Use of an inductively coupled plasma quadrupole mass spectrometer equipped with a dynamic reaction cell has been reported[10] for the accurate determination P^+ as the oxide ion $^{31}P^{16}O$ at m/z 47 that is less interfered.

Determination of phosphorus polarographically has been carried out by[11] as phosphate from the catalytic polarographic wave of the reduction of hydrogen peroxide in the presence of Mo(VI). Determination by potentiometric sensor has also been reported[5].

Absorptiometric determination of phosphorus in iron and steel also necessitates prior removal of interfering elements. Lindley[12] investigatigated vanadomolybdiphosphate method and Pakalns[13-14] extracted the yellow molybdophosphoric acid with isobutyl acetate and isobutyl methyl ketone and subsequently reduced to heteropoly blue and determined it spectrophotometrically. Bhargava et al.[15] also reduced this complex to molybdenum-blue and measured the absorbance at 725 nm.

Application of neutron application in the analysis of silicon, phosphorus, and sulphur in alloy steel involves rapid radiochemical separation procedures. Nadkarni & Haldar[16] reported a standard deviation and sensitivity limit for phosphorus as 2.3% and 0.20p.p.m. respectively. Heslop et al.[17] determined phosphorus in steel gravimetrically using radioisotopes of phohphorus-32 and arsenic-74 by the extraction of molybdophosphoric and molybdoarsenic acids from aqueous solution with n-butyl acetate.

In the present method, the steel sample is dissolved in 1:1 *(v/v)* HNO_3 and phosphorus is subsequently precipitated as silver phosphate. Colson[18] recommended the use of silver ion for the precipitation of phosphate and only 0.7% of added phosphorus had escaped precipitation. It is dissolved in cold and dilute HNO_3 and determined colorimetrically at 465 nm. This method is rapid, accurate and free from interference from alloying elements like nickel, vanadium, copper, manganese and molybdenum and chromium (III) oxidation stage but not from tungsten and chromium (VI).

EXPERIMENTAL

Reagents

EDTA solution (0.1 M) : 37.224 g of ethylenedinitrilotetraacetic acid disodium salt (dihydrate) ($C_{10}H_{14}N_2Na_2O_8.2H_2O$) GR grade Merck is dissolved in 1000 mL of deionised water.

Silver nitrate (3 % wt/v) solution : 3 g of silver nitrate ($AgNO_3$) AnalR grade is dissolved in 100 mL of deionised water (free from chloride ion) and stored in amber coloured bottle. This solution is kept in dark when not in use.

Ammonium vanadate-molybdate reagent : (a) 1 g of ammonium vanadate in about 300 mL of water is dissolved. To this 140 mL of HNO_3 (sp.gr.1.42) is slowly added. (b) 40 g of ammonium

molybdate $(NH_4)_6 Mo_7O_{24}.4H_2O$ is dissolved in 400 mL of deionised water. Before the experiment, about 45 mL of solution 'a' and 40 mL of solution 'b' are mixed and made upto 100 mL with deionised water.

Standard phosphate solution : 2.1965 g of potassium dihydrogen phosphate dried at 105°C is dissolved in 500 mL of deionised water. 5 mL of this solution is made upto 500 mL with deionised water. A 1 mL of this solution contained 0.01 mg of Phosphorus.

Standard iron solution : Electrolytic grade iron powder (99.0%) of Aldrich make has been dissolved to prepare 1000 mg/L in concentrated HNO_3. 1 mL of this solution contained 1.0 mg of iron.

pH meter : A digital pH meter of Systronics make, Model 335 has been used. Absorption studies were conducted in a Shimadzu UV-VIS spectrophotometer 2100S.

Determination of phosphorus in synthetic mixtures

Synthetic mixtures of iron containing 100 mg of iron and 0.01, 0.02, 0.04, 0.05 and 0.07 mg of phosphorus respectively were prepared in a 100 mL volumetric flask but the final volume was kept at about 80 mL. A 5.0 mL of EDTA (0.1 M) solution is added to each of the solutions and pH is adjusted to 4.0-5.0 with the help of a pH meter and now the volume is . Silver nitrate solution is added dropwise till the precipitation of yellow coloured silver phosphate is complete and it is filtered through a Whatman No.42 filter paper and subsequently dissolved in 8 mL of (1:10 HNO_3). A 2 mL of ammonium molybdo-vanadate reagent is added to the solution (so as to make the volume 10 mL)and the resulting yellow colour of ammonium phosho-molybdevanadate complex is measured at 440 nm. The results are plotted to construct a calibration curve (Fig. 1). A similar experimentation taking above mentioned amounts of phosphorus but with 200 mg of iron was carried out and the resulting absorbance plotted Fig. 2. Tolerance limit for vanadium and molybdenum has also been determined from synthetic mixture of composition 100 mg iron, 0.04 mg phosphorus and varying amount of vanadium and (1 to 5 mg) or molybdenum 0 to 2 mg.

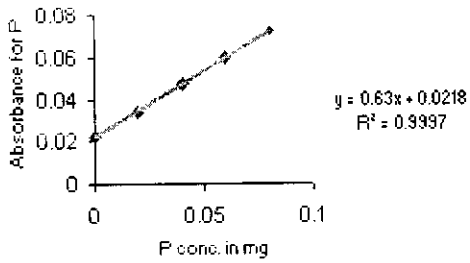

***Fig. 1** : Calibration curve for P in presence of Fe (100 mg)*

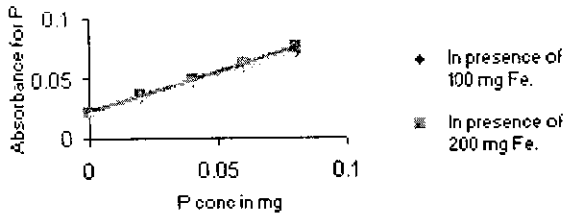

***Fig. 2** : Calibration curve for P in presence of Fe*

Determination of phosphorus in steel sample : The steel samples (0.15 to 0.2 g) after dissolution in (1:1) nitric acid solution is filtered and 10 ml of 0.1 M EDTA solution is added. Its pH is adjusted to 5.0 and silver nitrate solution (3% w/v) is added to precipitate phosphate ion. It is filtered and redissolved in dilute nitric acid (1:10). A 2 mL solution of ammonium molybdonvanadate solution is added and absorbance is measured of the resulting ammino-phospho-vanado-molybdate.

RESULTS AND DISCUSSION

From Fig.1 and 2, it is observed that ammonium molybdo-phospho vanadate obeys Beer's law when P is present in the concentration range 0 to 0.08 mg/ 100mL of the solution and iron is present 100 to 200 mg in the same volume of solution. Presence of vanadium (up to 5 wt%) and that of molybdenum (from 0 to 2 wt %) are tolerated as studied in the synthetic mixture (Table 1). However, hexavalent chromium added as dichromate seriously interferes in the measurement but if it is reduced to trivalent state this interference is removed (Fig. 3). The solubility product of $Ag_2Cr_2O_7$ and Ag_3PO_4 are respectively 2.0X 10 $^{-7}$ and 2.8 X 10^{-19}, respectively at 25° C. Therefore, in presence of excess of silver ion, Cr(VI) starts precipitating and contaminates the silver phosphate precipitate. In Fig.3 and Table 1, percent of phosphorus determined from

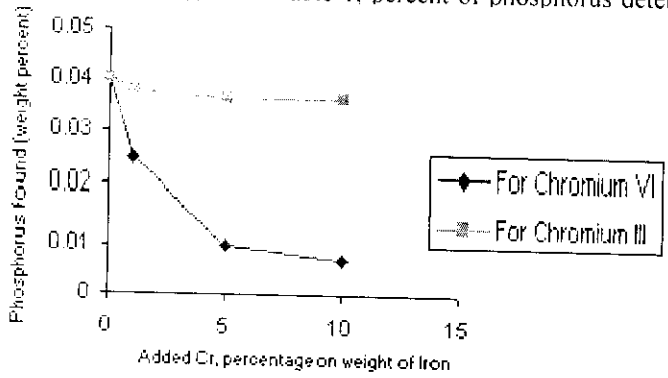

Fig. 3 : Effect of chromium

average of three measurements are reported. Here, Synthetic mixture have been used with a composition Fe(100 mg), P (0.04 mg), V (3.0 mg) and Mo (0.5 Mg) and varying amounts of Cr(VI) (0 to 10 mg) subsequently reduced to trivalent oxidation state in 100 mL solution. Here, the combined precipitate of silver chromate and that of silver phosphate was redissolved in dilute nitric acid (1:10 v/v) with subsequent addition of sulphurous acid to convert hexavalent chromium to trivalent state. As (V), if present, is also reduced to As(III) by sulphurous acid. In presence of tungsten a turbid solution is developed which seriously interferes in the estimation.

Table 1: Effect of chromium (VI) and (III) interference studies in a synthetic mixture of 100 mg of iron, 0.04 mg phosphorus, 3.0 mg vanadium, 0.5 mg molybdenum and varying amounts of chromium

Chromium added, Percent on weight of iron	Phosphorus found (%) in presence of Cr(VI)	Phosphorus found (%) in presence of Cr(III)
Nil	0.040	0.040
1.0	0.030	0.038
2.0	0.025	0.039
3.0	0.015	0.037
5.0	0.010	0.038
7.5	0.09	0.038
10	0.09	0.039

Table 2 : Comparison of the amount of phosphorus determined in some BCS reference steel samples.

Sl. No.	Standard No.	Description of standard	Phosphorus (wt.%)	Phosphorus determined (wt.%)	RSD %
1.	BCS-403	Low alloy Steel	0.064	0.0625 0.0620 0.0630 0.0640	2.22
2.	BCS-161/3	0.8% carbon steel	0.043	0.0425 0.0438 0.0432 0.0428	3.48
3.	BCS-163/2	1.2% carbon steel	0.019	0.0188 0.0185 0.0190 0.019	3.68
4.	BCS-211	13 % Cr-Steel	0.017	0.0165 0.0165 0.0175 0.0170	2.50

In Table 2, phosphorus determined by the present method in several BCS samples are reported. The RSD values lies ± 4.0%.In Table 3, results of several samples analysed by present method are given. These samples have also been analysed by IS 228 method and for comparision

Table 3 : Comparison of analysis results of some HT steel samples of Power Grid Corporation & steel samples of MPCL, as per IS 228 and present method (contains no tungsten)

Sl. No.	Sample description	Phosphorus (%) As per IS 228	Phosphorus (%) determined by Silver phosphate method
01.	Sample 1 (Power Grid)	0.034	0.036
02.	Sample 2 (Power Grid)	0.031	0.032
03.	Sample 3 (Power Grid)	0.036	0.034
04.	MPCIL steel	0.061	0.060
05.	As above	0.051	0.052

results obtained by the later procedure are also given. It shows that results are comparable. The rapidity of the present procedure can be enhanced if filtration procedure is replaced with centrifuge.

CONCLUSION

The present method separates out phosphorus from iron matrix by precipitating as silver phosphate, which is subsequently determined photometrically. The separation is quantitative as the value of solubility product is in the range of 10^{-18} and requires no repetition of this step unlike the solvent extraction method. This method has a drawback, as tungsten-bearing steel can not be analysed. Interference from chromium by reducing it to +3 Oxidation State has been achieved.

The tolerance limit for vanadium and that of molybdenum are such that most of the different type of steel samples can be analysed .The analysis can be completed within 2 to 3 hours which is much lesser than titrimetric procedure. If instead of filtration, centrifugation technique is adopted, the analysis time required is 30 minutes after acid dissolution of the sample.

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